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(19)

(54) DETERGENT COMPOSITION

(71) We, UNILEVER LIMITED, a company organised under the laws of Great Britain, of Unilever House, Blackfriars, London E.C.4, England, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement: —

The present invention relates to a detergent composition. More particularly it relates to an enzymic detergent composition that comprises lipolytic enzymes. The invention extends to the use of the compositions for soaking fabrics.

Enzymic detergent compositions are nowadays well known. The most common enzymic detergent compositions mainly contain proteolytic enzymes to remove stains and soil of proteinaceous nature. Often such compositions also contain amylolytic enzymes, since these are often present in commercial proteolytic enzyme preparations.

The inclusion in detergent compositions of enzymes of various types has been frequently proposed in the prior art. Proteolytic, amylolytic and inter alia also lipolytic enzymes have been suggested for inclusion in detergent compositions. However, the mere addition of lipolytic enzymes to any and all detergent compositions does not produce, as will be shown hereafter, a satisfactory and acceptable detergent composition, both regarding the enzymic activity and the cleaning efficiency. Various ingredients of detergent compositions have been found to exert a negative influence on lipolytic enzymes.

It has now been found that if lipolytic enzymes are used in conjunction with particular active detergent materials, which will be defined hereafter, a satisfactory cleaning efficiency is achieved without those detergent materials having a negative influence on the lipolytic enzymes. In some cases, which will be described hereafter, even a stimulation of the lipolytic enzymes is achieved.

The active detergent materials to be used according to the present invention are detergent surfactants that contain in their molecule an ethylene oxide or a propylene oxide chain containing an average of 3 to 10 and preferably of 5—9 moles of ethylene oxide, or propylene oxide. These detergent surfactants consist of either those which are known in the detergent art as nonionic detergent surfactants, or a sodium or potassium salt of a carboxylic acid derivative of such nonionic detergent surfactants. These active detergent materials should have a Hydrophilic-Lipophilic-Balance value of less than 14. The H.L.B. value is defined by ethylene oxide content (in %) divided by 5.

The nonionic detergent surfactants to be used according to the present invention are condensation products of from 3 to 10 moles of ethylene oxide with a hydrophobic organic compound such as primary, aliphatic monohydric alcohols containing from 8—25 carbon atoms; second arylaliphatic monohydric alcohols containing from 8—20 carbon atoms; alkylphenol containing from 8 to 18 carbon atoms in the alkyl group; fatty acid amides or alkylolamides containing from 10—18 carbon atoms in the fatty acid residue and so on. Further suitable examples of hydrophobic compounds that can be ethoxylated to produce nonionic detergent surfactants for use according to the present invention can be found in M. J. Schick, "Nonionic Surfactants", Vol. I 1967.

The derivatives of nonionic detergent surfactants which can be used according to the present invention are salts of carboxylic acid derivatives. For example, carboxylated derivatives of nonionic detergent surfactants as exemplified above may be used. These can be prepared, e.g. by treating the corresponding nonionic detergent surfactant with monochloroacetic acid and sodium or potassium hydroxide yielding sodium or potassium salts of alkyl or alkylaryl polyglycolether acetic acid.

Specific examples of suitable nonionic detergent surfactants to be used in the present invention are: nonylphenol condensed with 5 moles of ethylene oxide, nonylphenol condensed with 10 moles of ethylene oxide, secondary C_{11-15} alcohol condensed with 3, 7 or 9 moles of ethylene oxide (known under the registered trade name Tergitol® S ex Union Carbide Corp.). A specific example of derivatives of a nonionic detergent surfactant is sodium lauryl (4.5 moles of ethylene oxide) acetate.

The lipolytic enzymes to be used in the present invention are bacterial lipases produced by Pseudomonas strains, especially Ps. stutzeri ATCC 19154. In general, the preferred lipolytic enzymes should have a pH optimum lying between 6 and 10, and should be active in said range, preferably between 7 and 9. In general, the composition should contain from 5 to 90% by weight of the nonionic detergent surfactant or derivative thereof, and from 0.1 to 10% by weight of the lipolytic enzymes. Optimum results are obtained if the composition contains from 5 to 30% by weight of the particular detergent-active material and from 0.5 to 5% by weight of lipolytic enzymes. The compositions of the invention are particularly suitable for removing fatty material from fabrics. For example, the removal of fat stains from fabrics and fatty soil from cuffs and collars of shirts, blouses and the like often presents a problem to the housewife, requiring either a local treatment of the stain on the fabric with a spot-removing agent, or a separate manual pre-treatment of the cuffs and collars. In particular with mixed fabrics, consisting of a mixture of polyester and cotton, and especially coloured fabrics of this type, satisfactory removal of fatty soil is not easily obtained in a simple way. The compositions of the invention, however, satisfactorily remove fatty soil and can be used as a pre-washing or soaking composition at temperatures up to 60°C.

The present invention therefore particularly relates to a pre-washing or soaking composition comprising particular detergent-active materials and lipolytic enzymes. The soaking composition can satisfactorily remove fatty soil, and the lipolytic enzymes present in the composition are not negatively influenced, but sometimes even stimulated, by said particular detergent-active materials.

It has been found that optimum results are obtained with the combination of lipolytic enzymes from Pseudomonas stutzeri ATCC 19154 and a nonionic detergent surfactant consisting of secondary C_{11-15} alcohol condensed with 3—10 moles of ethylene oxide. After soaking a fabric soiled with fatty soil, for 1 hour at 45°C with this combination, a considerable higher fat removal can be obtained, compared with soaking in this composition without lipase. It has furthermore been found that in this particular combination up to 50% of the nonionic detergent surfactant can be replaced by sodium dodecylbenzenesulphonate, without a significant impairing effect on the lipolytic enzymes.

According to the invention the compositions of the invention are used in a process of soaking cotton and polyester/cotton fabrics in an aqueous solution between room temperature and 55°C.

The compositions of the invention may furthermore contain the usual detergent additives. Thus, they may contain phosphates, silicates, sulphates, carbonates, builders such as sodium tripolyphosphate and/or trisodium nitrilotriacetates; soil-suspending agents such as sodium carboxymethylcellulose; chelating agents such as EDTA; small amounts of other active detergents, e.g. sodium cocosoap (up to 1%); fluoroescers, perfumes, germicides, colouring agents and the like. Hydrotropes and wetting agents, such as sodium xylene- and toluene sulphonate; furthermore solvents and co-solvents such as dibutylphthalate may also be included. Proteolytic and/or amylolytic enzymes may also be added to the compositions. The invention will now be further illustrated by way of example with reference to the accompanying drawings in which Figure I contains graphs showing the activity of a lipase (ATCC 19154) at a range of concentrations of two nonionic surfactants and discussed in Example II and Figures IIa and IIb are graphs showing the activity of a lipase (ATCC 19154) with Tergitol 15—S—9 ('T' or 'Terg') and sodium dodecylbenzene sulphonate ('Dobs').

EXAMPLE I.

The following experiments were carried out.

A substrate was prepared from 2 g of olive oil, dissolved in 150 ml chloroform, to which 50 g of either a polyester/cotton mixture (65:35) with a particle size of less than 0.5 mm or a synthetic fibre, known under the trade name Terlenka® ex AKZO, Holland, with a particle size of less than 0.5 mm was added. This slurry was allowed to dry in the air, at room temperature, and stored in a refrigerator at 4°C.

2.0 g of this substrate was brought into a 50 ml, wide mouth glass-stoppered flask. 10 ml of an incubation medium, which was prepared by adding 2.5 g pentasodium tripolyphosphate and 1.78 g disodium mono hydrogen orthophosphate to 1 l water of 15° German hardness, the pH being adjusted to 8 with a 1 M aqueous solution of mono sodium dihydrogen phosphate, was added to the substrate in the flask. Subsequently 1 ml of an enzyme solution was added. This enzyme solution contained 100 mg lipase in 100 ml of water. After 16 hours at 25°C, the reaction was

stopped by adding 25 ml of ethyl alcohol, and the mixture was potentiometrically titrated with 0.1 N sodium hydroxide solution.

The analyses were carried out in duplicate, and the mean net titration values were expressed as micro equivalent of free fatty acid, representing the lipase activity under the test conditions. In these experiments, a lipolytic enzyme produced by Pseudomonas stutzeri ATCC 19154, and as nonionic detergent surfactants sec. C_{11-15} alcohol condensed with 3 or 9 moles of ethylene oxide were used.

The results are shown in Figure I.

In Figures IIa and IIb the results are shown of the same procedure, in which mixtures of sec. C_{11-15} alcohol, condensed with 9 moles of ethylene oxide, (Tergitol® 15—S—9) and sodium dodecylorthobenzenesulphonate (DOBS—JN) in various ratios are used as detergent surfactant.

Figure I clearly shows a stimulating effect of the nonionic detergent surfactant on the lipolytic enzyme, and Figures IIa and IIb show that within particular ratios the stimulating effect of said nonionic detergent surfactant can be increased by the addition of sodium dodecylorthobenzenesulphonate. Tergitol 15—S—9 is secondary C_{11-15} alcohol condensed with nine moles of ethylene oxide.

EXAMPLE II.

Soaking and washing experiments were carried out as follows:

Test pieces of a fabric, consisting of 65% polyester and 35% cotton were soiled with 3—4% by weight of the fabric of a 1:1 mixture of glyceryltripalmitate and glyceroltrioleate. This mixture contained a small amount of β-1-^{14}C oleoyl labelled glyceryl oleate and 9-10-^{3}H labelled glyceryl-palmitate in a ratio of 1:4. These soiled test pieces were soaked, washed and rinsed in a Tergotometer under the following conditions:

Conditions	Soaking	Washing	Rinsing
time	16 h	20 min.	3 min.
agitation	1 min at 60 rpm at the start of the soaking process	60 rpm	60 rpm
temperature	ambient temperature	50°C.	in 3 min from 20—38°C.
cloth/liquor ratio	1 : 50	1 : 50	1 : 50
solutions used	3.5 g/l of products[x]) in water of 15° German hardness	5 g/l of product B[xx]) in water of 15° German hardness	water of 15° German hardness
pH	8	9.3	

[x])The soaking solutions consisted of 3.5 g/l of the following composition

	% by weight
pentasodiumtripolyphosphate	40
disodiumdihydrogenpyrophosphate	11
sodium silicate ($Na_2O : SiO_2 = 1 : 3.5$)	2.4
sodium sulphate (anhydrous)	39.7
ethylenediaminetetraacetic acid	0.24
sodiumcarboxymethylcellulose (100%)	1.5
water	balance

which additionally contained the following constituents:

Series A: 70 mg/l of a commercially available lipase ex Meito Sangyo Co., Japan, called Lipase My 10,000, a microbial lipase from Candida cylindracea nov. Sp. and 0, 0.125, 0.25 or 0.5 g/l of a nonylphenol condensed with 5, 10 or 14 moles of ethylene oxide or a secondary C_{11-15} alcohol condensed with 3,7,9 and 17.4 moles of ethylene oxide.

Series B: the same as series A, but with the difference that 70 mg/l of a more active lipase ex Meito Sangyo Co., called Lipase My 30,000, also contained from Candida cylindracea nov. Sp., was used.

[xx])The washing solutions consisted of 5 g/l of the following composition:

	% by weight
tallow alcohol condensed with 25 moles of ethylene oxide	7.4
sodium coconut oil soap	1.1
sodium tripolyphosphate	45.3
sodium silicate ($Na_2O : S_1O_x = 1 : 3.5$)	2.1
sodium sulphate (anhydrous)	35.3
ethylenediaminetetraacetic acid	0.21
sodium carboxymethylcellulose	1.4
water	balance

The percentage of fat removal was calculated with the aid of the radiotracers (simultaneous measurement of ^{3}H-tripalmitate and ^{14}C-trioleate). All experiments were carried out in triplicate.

Soaking was carried out at 20, 35 and 45°C for 1, 4 and 16 hours. The nonionic active detergent used was sec. C_{11-15} alcohol condensed with 7 moles of ethylene oxide. The lipase used was a bacterial lipase from Psuedomonas stutzeri ATCC 19154. The results were as follows and demonstrate that soaking, particularly over prolonged periods, with compositions of the invention yielded significantly better fat removal than compositions not containing lipase.

Soaking conditions			Fat removal			
			% Trioleate removed		% Tripalmitate removed	
Time	Temp. (°C.)	Concentration nonionic active detergent added (g/l)	without lipase	with 79 mg/l lipase	without lipase	with 70 mg/l lipase
1	20	—	7	7	8	7
		0.125	3	9	4	7
		0.25	6	15	7	13
		0.50	16	23	15	12
	35	—	2	4	7	5
		0.125	15	17	13	14
		0.25	14	31	10	26
		0.50	21	32	17	29
	45	—	7	26	5	22
		0.125	11	39	11	34
		0.25	9	38	8	34
		0.50	15	37	15	33
4	20	—	12	8	13	7
		0.125	19	35	21	26
		0.25	17	41	17	31
		0.50	21	47	20	32
	35	—	4	38	5	26
		0.125	9	43	8	30
		0.25	15	52	11	34
		0.50	21	51	15	34
	45	—	5	39	3	35
		0.125	16	54	15	52
		0.25	21	52	21	49
		0.50	22	55	20	52
	20	—	8	16	9	11
		0.125	8	63	10	38
		0.25	9	63	19	38
		0.50	26	67	20	42

Soaking conditions			Fat removal			
			% Trioleate removed		% Tripalmitate removed	
Time	Temp. (°C.)	Concentration nonionic active detergent added (g/l)	without lipase	with 79 mg/l lipase	without lipase	with 70 mg/l lipase
16	35	—	9	62	8	44
		0.125	17	79	17	55
		0.25	26	79	20	52
		0.50	30	81	21	64
	45	—	6	66	7	64
		0.125	11	82	11	75
		0.25	29	84	28	74
		0.50	33	84	30	70

WHAT WE CLAIM IS:—

1. A detergent composition comprising bacterial lipolytic enzymes derived from Pseudomonas strains and a nonionic detergent surfactant which contains from 3 to 10 moles of an alkylene oxide with from 2—3 carbon atoms in its molecule, or a sodium or potassium salt of a carboxylic acid derivative thereof.

2. A composition according to claim 1, in which the nonionic detergent surfactant or a derivative thereof contains from 5 to 9 moles of ethylene oxide.

3. A composition according to claim 1 or 2, in which the nonionic detergent surfactant is sec. C_{11-15} alcohol condensed with 3, 7 or 9 moles of ethylene oxide.

4. A composition according to claim 1 or 2, in which the nonionic detergent surfactant is nonylphenol condensed with 5 or 10 moles of ethylene oxide.

5. A composition according to claims 1—4, in which the bacterial lipolytic enzymes are derived from Pseudomonas stutzeri ATCC 19154.

6. A composition according to claims 1—5, comprising a mixture of sec. C_{11-15} alcohol condensed with 3 to 10 moles of ethylene oxide, and calculated on the amount of nonionic detergent surfactant, up to 50% by weight of sodium dodecyl benzene sulphonate.

7. A process for soaking cotton and polyester/cotton fabrics, comprising applying an aqueous solution of a composition according to claims 1—6 to the fabrics at a temperature between room temperature and 55°C.

8. A detergent composition as claimed in claim 1 substantially as herein described.

9. A detergent composition as claimed in claim 1 substantially as described in any of the Examples.

10. A process for soaking cotton and polyester/cotton fabrics as claimed in claim 7 substantially as herein described.

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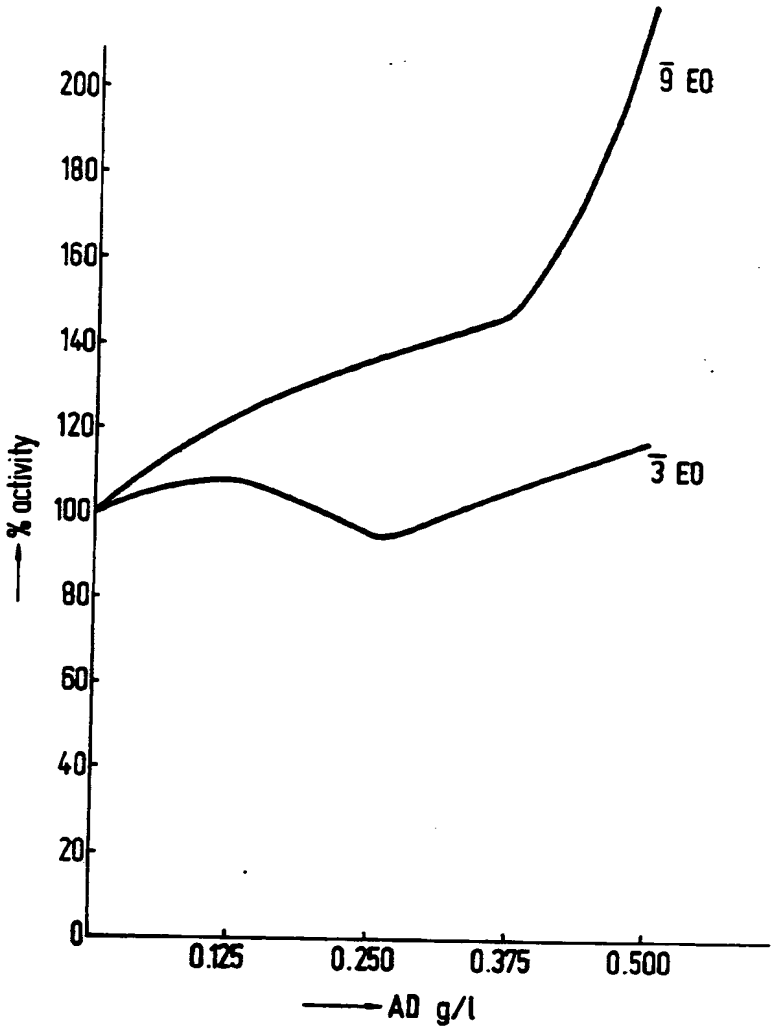
FIG.I


200
180
160
140
120
100
80
60
40
20
0
% activity
9 EO
3 EO
0.125
0.250
0.375
0.500
AD g/l

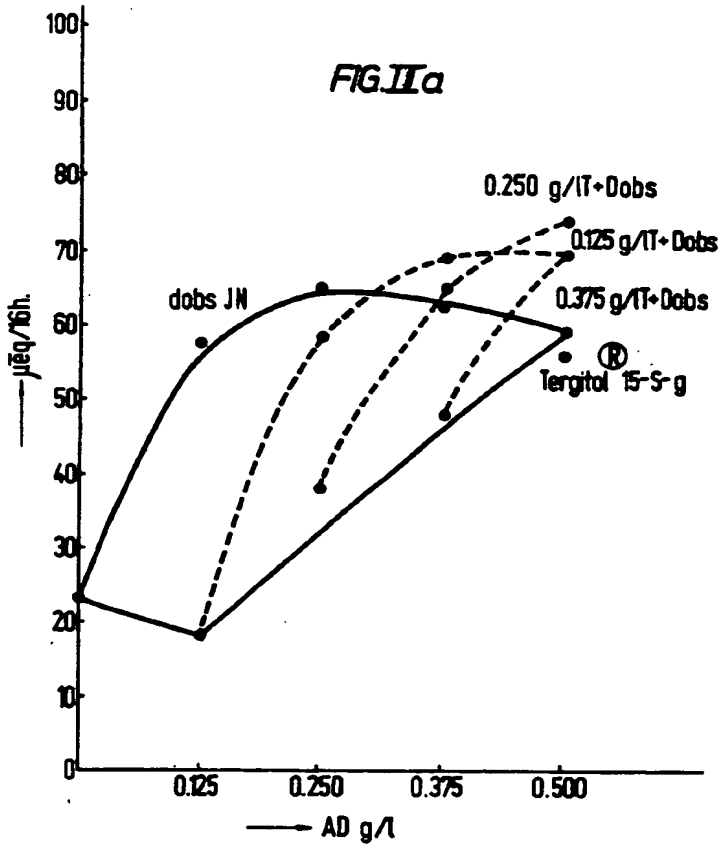
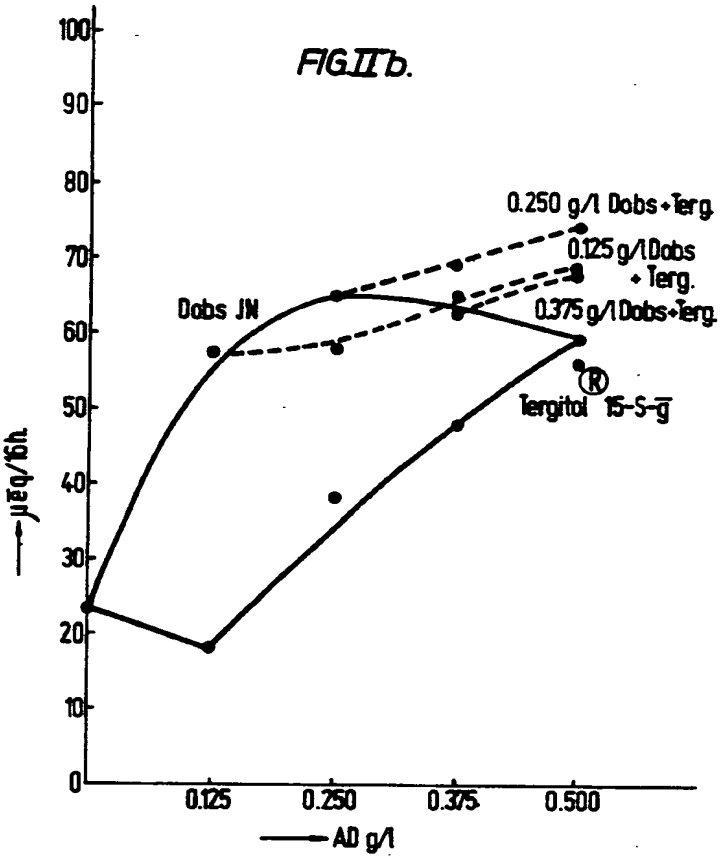


FIG.IIa
100
90
80
70
60
50
40
30
20
10
0
0.125
0.250
0.375
0.500
—µéq/16h.
—— AD g/l
0.250 g/lT+Dobs
0.125 g/lT+Dobs
0.375 g/lT+Dobs
dobs JN
Tergitol 15-S-g

FIG.II b.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90
80
70
60
50
40
30
20
10
0
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0.250 g/l Dobs+Terg.
0.125 g/l Dobs + Terg.
0.375 g/l Dobs+Terg.
Dobs JN
Tergitol 15-S-9
0.125
0.250
0.375
0.500
—AD g/l